

# Pt/laponite clay-modified gold electrode for direct methanol fuel cells

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Received: 27 March 2012 / Accepted: 5 May 2012 / Published online: 22 May 2012  
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**Abstract** This work employs a novel technique in which laponite clay-modified gold electrodes are used as the anode for direct methanol fuel cells. The platinum/laponite clay (Pt/Clay) films on indium tin oxide electrode were characterized by using scanning electron microscope and energy-dispersive X-ray spectroscopy. Various contents of laponite clay (0.1, 0.5, 1.0, and 2.0 wt%) with constant platinum (Pt) catalyst content on modified gold electrodes were studied as an anode catalyst for methanol oxidation. The catalyst poisoning was observed as a function of time. The 1.0 wt% Pt/Clay-modified gold electrode shows the highest activity for methanol oxidation, 27.73 % higher than Pt only modified gold electrode at 2.5 min. The peak current of 1 % Pt/Clay-modified gold electrode is 3.50 % higher than the peak current of Pt only modified gold electrode at 57.5 min. The higher content of Pt/Clay-modified gold electrode shows strong resistance to catalyst poisoning. The Pt/Clay-modified gold electrode is a new and promising electrode for a direct methanol fuel cell and can replace existing commercial catalysts.

**Keywords** Direct methanol fuel cells · Pt/Clay film · Gold electrode · Pt catalyst · Clay

## 1 Introduction

One of the most important energy security and environmental goals over the next few years will be using bio-fuels such as methanol and ethanol. Direct methanol fuel cells (DMFC) have attracted considerable attention due to the

application as a bio-fuel power resource [1, 2]. It has advantages because it is easy to handle and it does not require for a complex reformer unit in comparison to the H<sub>2</sub> fed polymer electrolyte membrane fuel cell. Methanol fuel cells offer significant savings of loads, in weight and volume compared to conventional power sources. It can be used in portable power applications such as commercial electronics and battery replacement for the military and transportation. Today, one of biggest hurdles for DMFC to reach commercialization is still requisite of a significant amount of platinum catalysts to achieve an acceptable power density. Platinum (Pt) is the most promising catalyst but the Pt surface is seriously poisoned in the presence of a trace amount of carbon monoxide (CO) because methanol can be easily dehydrogenated in DMFC [3, 4]. The CO poison is not oxidized away unless the anode potential is increased to greater than 0.6 V, which causes a net result of increased loss of cell voltage and efficiency. The less expensive and more abundant non-platinum catalysts that can offer better performance have been investigated [5, 6]. Several heterogeneous catalysts for methanol oxidation were studied in recent years with gold nanoparticles and metal oxides [7, 8]. Extensive research has been conducted by using binary and ternary catalysts for oxidation of CO in fuel cell [9–12]. A promoter is required to weaken CO bonding on Pt to catalyze CO oxidation in the binary and ternary catalysts such as Pt/Ru alloy [13, 14]. However, Ru, a natural resource, is limited by the availability; and inadequate in high CO concentrations, better substitutes are being sought [15, 16].

Of novel interest is the application of clay–organic complexes as an electrode modifier. Metal complexes incorporated into a clay film are known to be electrochemically active. Thus, clay-modified electrodes (CMEs) have attracted the attention of many electrochemists because of the ion-exchange properties of the clay and because of the unique

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layered structure of the material. The smectite group of clay minerals, exhibits ion-exchange properties and intercalation into an interlayer space, but are electrochemically inactive. However, dilute aqueous smectite suspensions are well suited to convert into electrochemically active nanofilms. The functionalization is performed by ion exchange of amphiphilic molecules carrying the desired functionality. A functionalized clay mineral nanofilm is obtained by the organization of the molecules at the clay surface and by the organization of the elementary clay platelets in the film. The CME is prepared by covering an electrode (e.g., glassy carbon, SnO, glass, and platinum) with a thin film of aqueous clay dispersion ( $<1\text{ }\mu\text{m}$  in thickness) [17]. The electrode shows reversible redox currents in cyclic voltammetry due to the incorporated metal complex. Usually, one challenge of the preparation is accurately controlling the thickness of the film. However, Hotta et al. report that using the Langmuir–Blodgett method, to form a thin film at an air–water interface with the clay ion-exchanged by an alkylamine, it is possible to prepare a clay film with controlled thickness on a molecular scale. Electroactivity of the films of clay–organic complexes was further confirmed. Low electronic conductivity of clay minerals causes electron transport in CME to depend on a combination of diffusion of the adsorbates through the films, and electron hopping between adsorbed species [18]. The limited mobility of cations in clay films means that, only those that are adsorbed in the vicinity of defects in the film structure can reach the conductive substrate to participate in the electrochemical reaction. Where this confinement is desired, smectite clays receive considerable attention. On the other hand, clay minerals such as montmorillonite are layered silicates, able to exchange cationic ions and intercalate neutral molecular species between the interlayer regions [19, 20]. Clay is easy to obtain and much less expensive than precious metals. The clay layer can attract more Pt nanoparticles to improve surface area [21–23].

In this study, we present for the first time that clay-modified Pt nanoparticle was used as an anodic catalysts and successfully applied in the high performance of DMFC. The Pt/Clay catalysts were composed of various percent of clay (0.1, 0.5, 1.0, and 2.0 wt%) and a constant amount of Pt catalyst. The Pt/CME showed an enhanced in the performance of DMFC and reduced poisonous effect at 1 wt% of clay. This modification approach could be a new promising electrode in the fabrication of direct methanol fuel cell.

## 2 Experimental section

### 2.1 Reagents and instruments

Hydrogen hexachloroplatinate ( $\text{H}_2\text{PtCl}_6$ ), methanol, hydrogen peroxide, and sulfuric acid were used as received

from Sigma-Aldrich and all were analytical grade or better. Laponite clay was obtained from Conservation Resources International, LLC which has platelet structure about 25 nm in diameter. The gold electrodes (diameter 1 mm) were purchased through CH Instruments, Inc. Electrochemical measurements were carried out using an electrochemical analyzer (CHI 440A, CH instruments Inc., USA). Scanning electron microscopy (SEM) images were obtained with a Zeiss 1450EP variable pressure SEM operating at 20 kV in HV mode. EDX was performed by the LEO982 FE-SEM/EDX for elemental analysis of the samples.

### 2.2 Preparation of Pt/Clay-modified gold electrode

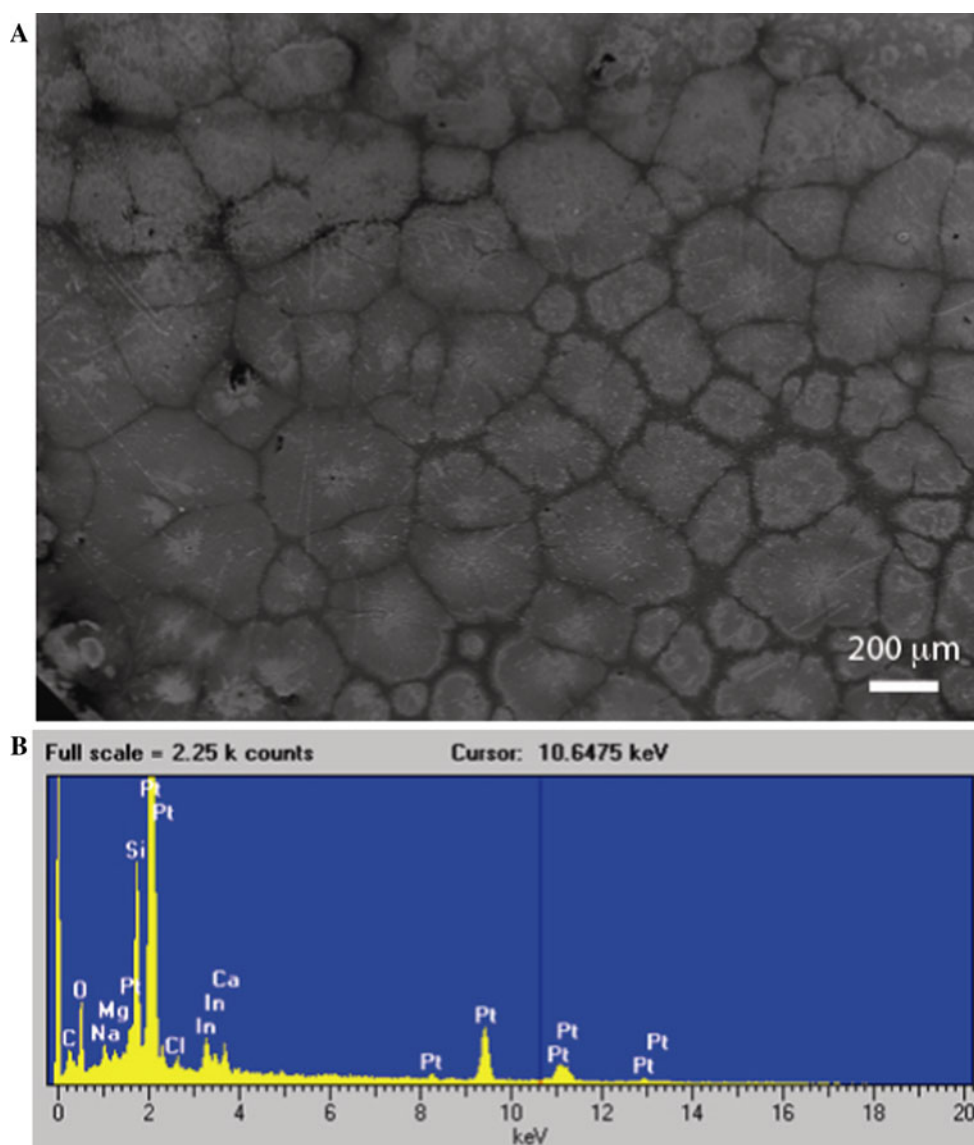
The surface of laponite clay is negatively charged, but their edges are either neutral or positively charged. As a result, they repel each other in the suspension and distribute evenly throughout the solution. Dispersions of 0.1, 0.5, 1.0, and 2.0 wt% laponite clay solutions in water were prepared. Then 9 ml of laponite clay solutions were mixed with 1 ml of 0.1 M  $\text{H}_2\text{PtCl}_6$ . A 1 ml portion of the Pt/Clay solution is then dispersed in 9 ml of 0.5 M  $\text{H}_2\text{SO}_4$  to obtain the final solution. The gold electrodes were cleaned with piranha solution (25 % hydrogen peroxide and 75 % sulfuric acid) for 15 s and then rinsed with distilled water and dried with nitrogen gas ( $\text{N}_2$ ). The Pt/Clay-modified gold electrode was obtained by electrochemical deposition using cyclic voltammetry (CV). The CV was performed from a potential of  $-0.2$  to  $0.7\text{ V}$  with a scan rate of  $100\text{ mV/s}$  for a total of 50 cycles. In a three-compartment cell, Pt wire is used as counter electrode and Ag/AgCl electrode is used as reference electrode. The test solution consisted of 1 M  $\text{CH}_3\text{OH}$  in 0.5 M  $\text{H}_2\text{SO}_4$ . Nitrogen was purged into the solution for 5 min. With the nitrogen protection, the cyclic voltammogram is measured as a function of time.

## 3 Results and discussion

### 3.1 Characterization of the Pt/Clay film

To characterize the Pt/Clay films, SEM was performed on the Pt/Clay films as shown in Fig. 1a. The films were prepared on ITO glass substrates with the same CV conditions as on the gold electrodes as discussed earlier. As can be seen from the SEM image, clay islands had formed on the ITO substrate measuring from 100 to 300  $\mu\text{m}$ . These islands were separated by less than 10–20  $\mu\text{m}$ . Analyzing the films with EDX showed a considerable amount of Pt present in the laponite clay samples as can be seen in Fig. 1b.

**Fig. 1** **a** SEM micrograph ( $\times 500$ ) of 2 % Pt/Clay films electrodeposited onto ITO glass substrates. **b** EDX analysis of 1 wt% Pt/Clay sample

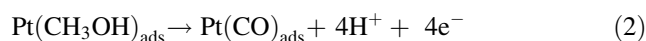
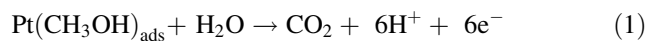


### 3.2 Electrochemical response of methanol on the Pt/Clay-modified gold electrode

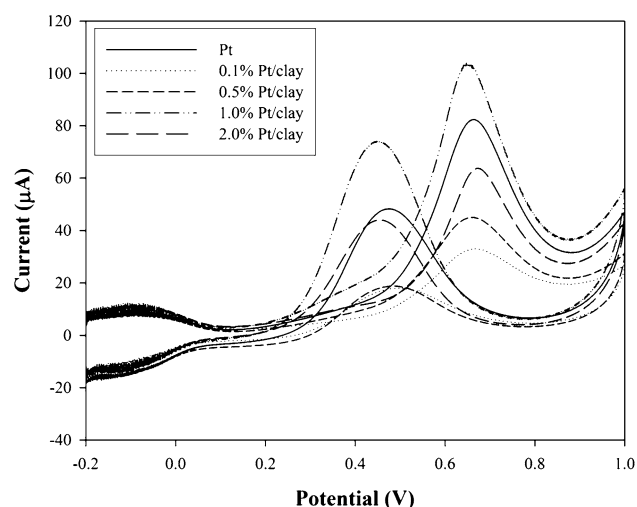
The activities of the Pt/Clay-modified gold electrode for the electrooxidation of methanol were investigated in a half-cell reaction. Since gold electrode possessed higher electron transfer rate compare to the conventional glassy carbon electrode, all the characterizations of methanol oxidation were investigated under the Pt/Clay-modified gold electrode [24]. A focused study of the effect of clay percentages of modified electrode for methanol oxidation is shown in Fig. 2. The current of methanol oxidation is increased by the percentage of laponite clay. The highest current was obtained at 1.0 wt% Pt/Clay-modified gold electrode. The lowest current was obtained at 0.1 wt% Pt/Clay-modified gold electrode. With the increase of laponite clay concentration to 1.0 wt%, the total surface

area of clay particles increases and the catalytic activity increases. When clay concentration is more than 1 wt%, the clay particles aggregate together, the real surface area will decrease; hence the decrease in the peak current.

Another important feature that must be analyzed for an electrocatalyst is its affinity to accumulate carbonaceous species. Electrooxidation of methanol to  $\text{CO}_2$  can occur via two mechanisms consisting of non-CO and adsorbed CO reactive intermediates [25]:



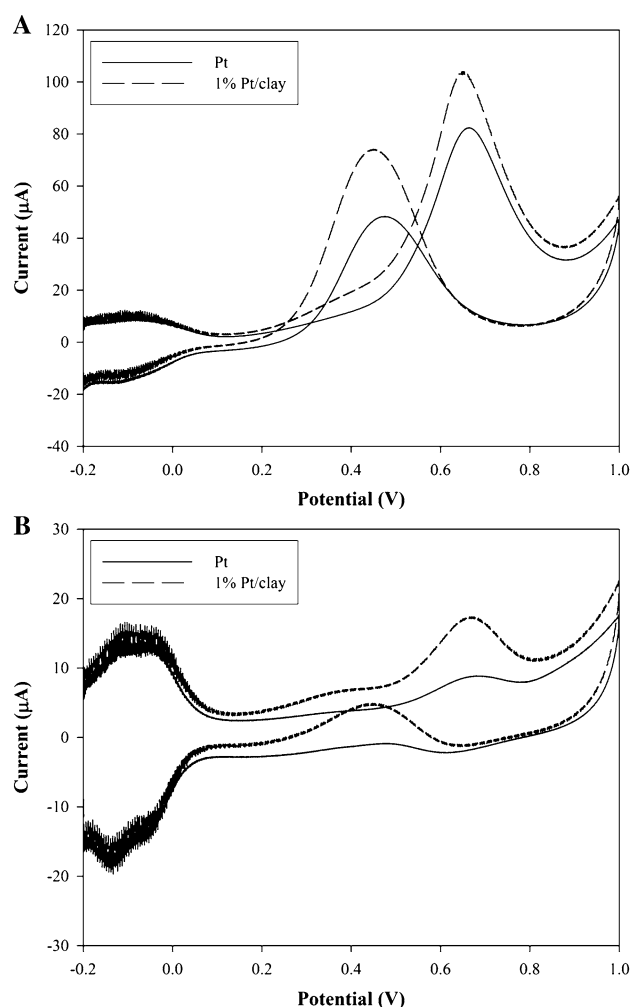
The non-CO reaction pathway (Eq. 1) is preferred for methanol oxidation since it does not involve CO, a poison for Pt. The adsorbed CO reaction pathway (Eq. 2) has intermediates mostly in the form of linearly bonded CO,



**Fig. 2** Cyclic voltammograms of 1 M methanol in 0.5 M  $\text{H}_2\text{SO}_4$  solution on Pt only, and different amounts of clay in the Pt/Clay-modified gold electrodes at 2.5 min

i.e.,  $\text{Pt}=\text{C}=\text{O}$ , which leads to CO poisoning of the Pt surface. During the reverse scan in the electrooxidation of methanol, the anodic peak is attributed to the removal of intermediate carbonaceous residues formed on the catalyst during the forward scan. Hence,  $I_F/I_R$ , the ratio between peak current of the forward scan ( $I_F$ ) and peak current of the reverse scan ( $I_R$ ) was used to evaluate the catalyst susceptibility to poisoning [26]. For commercial Pt/C electrode, the ratio of  $I_F/I_R$  is 0.77, indicating a significant number of methanol molecules are only partially oxidized in the forward scan. As shown in Table 1, the most efficient conversion of MeOH was occurring with the 0.5 % Pt/Clay-modified gold electrode as the reverse peak current was small compared to the forward peak current. The  $I_F/I_R$  ratio of the 0.5 wt% Pt/Clay-modified gold electrode was measured at 2.3, significantly higher than the Pt only modified gold electrode which had a ratio of only 1.68.

Figure 3 shows cyclic voltammograms of 1 M methanol in 0.5 M  $\text{H}_2\text{SO}_4$  solution with 1 wt% Pt/Clay and Pt-modified gold electrodes at 2.5 min (Fig. 3a) and 57.5 min (Fig. 3b), respectively. The current of 1 %

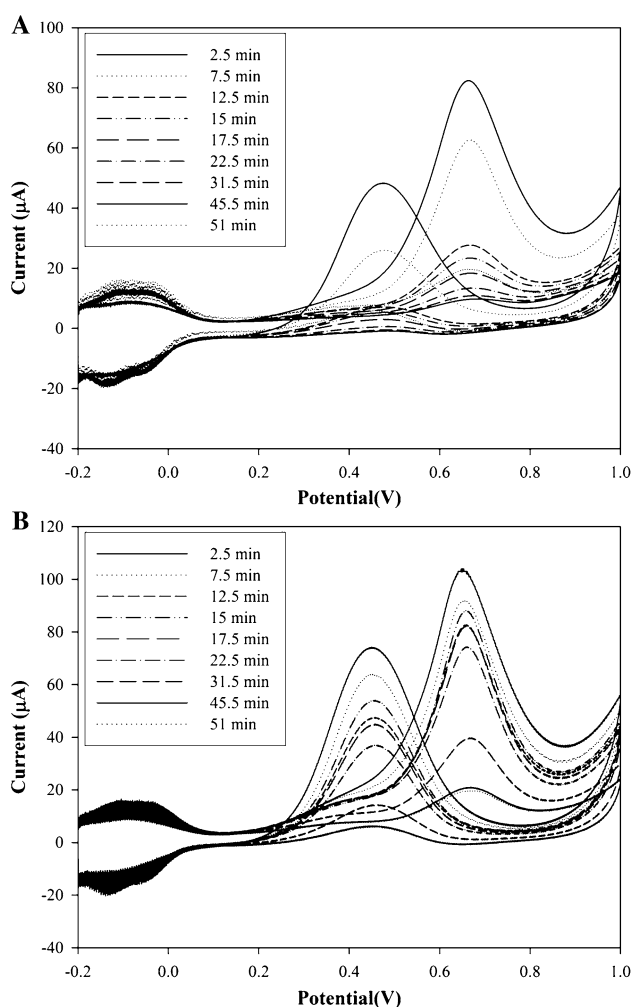


**Fig. 3** Cyclic voltammograms of 1 M methanol in 0.5 M  $\text{H}_2\text{SO}_4$  solution with 1 wt% Pt/Clay-modified gold electrodes at **a** 2.5 min and **b** 57.5 min. The catalyst effect in methanol oxidation of Pt/Clay-modified gold electrode is compared with Pt only modified gold electrode

Pt/Clay-modified gold electrode is larger than that of Pt only modified gold electrode. The relative large clay nanoparticle is anionic with large surface area, so clay particle attract more platinum cation due to the interaction of cation and anion; moreover, clay has good electron transfer ability. As exhibited, the 1 wt% Pt/Clay-modified gold electrode shows high catalytic activity. In general, high active surface area and high dispersion of the nano-catalyst on the substrate results in a large electrochemical active area for methanol oxidation. From Fig. 4a, the current peak decreases due to CO poison. Thus, the catalyst effect in methanol oxidation of Pt only modified gold electrode is shown. The current decreases with the increase of time due to the poison effect of CO and the decrease of methanol concentration. However, the Pt/CME still exhibit larger anodic currents, reflecting a relative lack of surface site blocking by CO. The catalyst effect in methanol

**Table 1** Peak current ratios of forward scan ( $I_F$ ) to reverse scan ( $I_R$ )

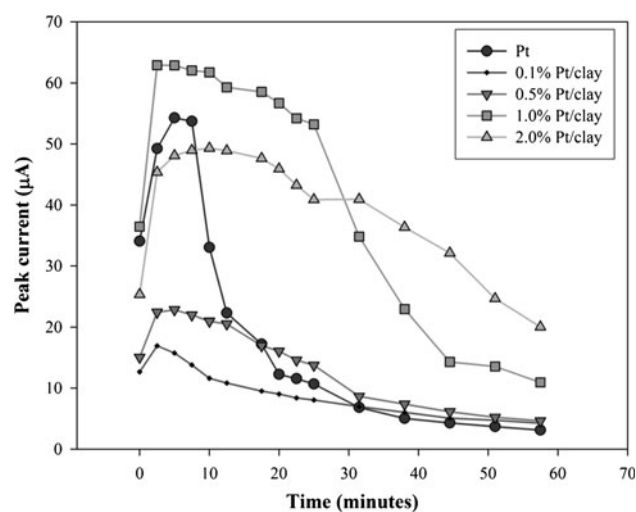
	Peak current ( $\mu\text{A}$ )		$I_F/I_R$
	Forward	Reverse	
Pt	80.7	47.9	1.68
0.1 % Pt/Clay	32.8	17.9	1.83
0.5 % Pt/Clay	44.8	18.8	2.38
1.0 % Pt/Clay	103	72.8	1.41
2.0 % Pt/Clay	61.7	43.7	1.41



**Fig. 4** Cyclic voltammograms of 1 M methanol in 0.5 M  $\text{H}_2\text{SO}_4$  solution with **a** Pt only and **b** 1 wt% Pt/Clay-modified gold electrodes

oxidation of 1 % Pt/Clay-modified gold electrode is shown in Fig. 4b. The current decreases too as a function of time but the 1 % Pt/Clay-modified gold electrode shows a high resistant to CO effect, which means clay decreases CO effect to the catalyst.

The trend of current peak as a function of time is shown in Fig. 5. The current peak decreases with the increase of time. For 0.1, 0.5, 1 wt% Pt/Clay and Pt only modified gold electrode, the current peak is higher with higher concentration of clay. For 2 wt% Pt/Clay-modified gold electrode, the current peak is higher than other at the first 10 min, then lower than that of 1 wt% Pt/Clay-modified gold electrode due to aggregation effect. In addition, as can be seen from Fig. 5, the rate of change in the current peak for the Pt/CMEs is substantially lower compared to the standalone Pt-modified electrode. This demonstrates the Pt/Clay catalyst acts to hinder CO poisoning of the active sites, thereby making it a more effective catalyst compared to Pt alone. Moreover, as shown in Fig. 5 the most



**Fig. 5** The peak current of 1 M methanol in 0.5 M  $\text{H}_2\text{SO}_4$  solution as a function of time with various content percentage of clay in Pt/Clay and Pt only modified gold electrodes

significant decrease in the peak current occurs after 30 min especially with the 1 and 2 wt% Pt/CMEs. The other Pt/Clay electrodes show a saturation effect after 30 min in which little change is observed in the peak currents. This may be due to the fact that fewer sites are available for methanol oxidation as using less clay reduces the realized surface area of the electrodes in the case of the 0.1 and 0.5 wt% Pt/Clay electrodes and the Pt only electrode.

Furthermore, the 1.0 wt% Pt/CME shows the highest activity for methanol oxidation, 27.73 % higher than Pt only modified electrode at 2.5 min. The peak current of 1 % Pt/CME is 3.50 % higher than the peak current Pt only modified electrode at 57.5 min. All the Pt/CMEs exhibited higher peak currents compared to the Pt only modified electrode after 30 min, illustrating the laponite clay's ability to produce more catalytic binding sites when used in conjunction with Pt nanoparticles. Although the 1 wt% Pt/CME had the largest peak current initially, after 30 min the 2 wt% Pt/Clay electrode showed greater activity. This can be contributed to the fact that with greater clay content more Pt active sites are still available for binding even after elapsed time and hence CO poisoning.

#### 4 Conclusions

The purpose of this project was to create a catalyst using a Pt/Clay-modified gold electrode that has a high catalytic activity for methanol oxidation and also resistant to catalyst poisoning. This involved the development of a Pt/Clay catalyst as an anode catalyst which plays a critical role in the high performance of DMFC. In this work, Pt/Clay catalysts were composed of various percent of clay



(0.1, 0.5, 1.0, and 2.0 wt%) and a constant amount of Pt catalyst. The Pt/Clay-modified gold electrode enhanced the performance in DMFC. The 1 wt% Pt/CME increases the catalytic activity and reduces the effect of CO poisoning. The anodic current of the 1 wt% Pt/Clay electrode measured as a function of time was more pronounced compared to the other electrode compositions of 0.1, 0.5, 2 wt% Pt/Clay and Pt only. This demonstrates that the 1 wt% Pt/CME has the largest surface area for catalytic binding. In addition, the 1 wt% Pt/Clay electrode showed the highest initial activity; 27.7 % higher than the Pt only electrode after 2.5 min, and 3.50 % higher after 57.5 min. However, the most efficient conversion of methanol was observed using the 0.5 % Pt/Clay electrode composition. The reverse peak current of the 0.5 wt% Pt/Clay composition was small compared to the forward peak current resulting in an  $I_F/I_R$  ratio of 2.3, significantly higher than the Pt only modified electrode which had a ratio of only 1.68. As demonstrated in this paper, Pt/Clay-modified gold electrodes are a new and promising anode for use in DMFC.

**Acknowledgments** Dr. Seong S. Seo would like to thank Dr. Minh-Puong N. Bui for his assistant for making the final manuscript.

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